

# THE FIRST LAW OF THERMODYNAMICS

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## 2.1 INTRODUCTION

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In the previous unit you were introduced to the domain of energetics as the study of energy in terms of its flow and transformation between a system and its surroundings. In chemical energetics we focus our attention on the flow and transformation of energy within chemical systems or between the chemical systems and their surroundings. You have learnt about the basic aspects of thermodynamics like its definition, importance, and terminology etc. You have also learnt about the concept of thermal equilibrium and the Zeroth law of thermodynamics as its consequence. In this unit, we are going to take up the First law of thermodynamics.

We would begin by explaining the concept of internal energy and then use it to state and explain the first law of thermodynamics. This would be followed by the description of heat changes under different conditions. Here, we would introduce the concept of enthalpy and then relate internal energy and enthalpy with the measurable quantity-heat capacity. We would also establish a relationship between the heat capacities at constant volume and at constant pressure. We would then apply the first law of thermodynamics to the gaseous systems undergoing expansion under isothermal and adiabatic conditions.

In the next unit we would take up thermochemistry-application of the first Law of thermodynamics to the heat changes accompanying chemical reactions and their measurement.

## Expected Learning Outcomes

After studying this unit, you should be able to:

- ❖ define internal energy;
- ❖ define and differentiate between the state functions and path functions;
- ❖ give different statements of the First Law of thermodynamics;
- ❖ formulate a mathematical expression for the first law of thermodynamics;
- ❖ discuss heat changes under constant volume and constant pressure conditions;
- ❖ explain the concept of enthalpy, its significance and the relationship with internal energy;
- ❖ relate the  $\bar{C}_p$  and  $\bar{C}_V$  respectively with enthalpy and internal energy;
- ❖ derive the relationship between  $\bar{C}_p$  and  $\bar{C}_V$  for an ideal gas;
- ❖ derive mathematical expressions for the work of expansion of gases under isothermal and adiabatic conditions; and
- ❖ establish relationships between different state variables for adiabatic expansion of an ideal gas.

## 2.2 THE FIRST LAW OF THERMODYNAMICS

You have learnt in the previous unit that heat and work are forms of energy in transit. Further, we know that a system may do work or the work is done on the system; accompanied by some energy transfer from or to the system. Similarly, we may give heat to the system or the system gives heat to the surroundings; again there is some energy transfer to or from the system. The question arises that when the energy (as heat or work) goes to the system where does it go? What change does it bring to the system? Similarly, when the system loses energy by doing work or by increasing temperature in the surroundings; what changes occur in the system? How do we represent such changes? In order to answer these questions we need to bring in the concept of internal energy symbolised as  $U$ .

### 2.2.1 Internal Energy, $U$

**Internal energy** is the energy possessed by a given system by virtue of its very existence and is composed of all possible types of energies, which all the constituents of the system put together can have. For example, chemical,

The internal energy does not include the kinetic energy due to the translation motion of the system as a whole.

The internal energy is an extensive property however; the internal energy per mole i.e., the molar internal energy is an intensive property. Like heat, and work the internal energy is also measured in the units of energy, joule.



**James Prescott Joule**  
(1818-1889)

In 1840s English physicist, **James Prescott Joule** (1818-1889) performed the experiments described in the text, in different ways like by rotating a paddle wheel, passing electric current, causing friction etc. He found that a given amount of work done on the system, irrespective of how it is done, produced the same change of state. The change in state was measured by the change in the temperature of the system. Thus, to produce a given change of state, the adiabatic work required is independent of the path by which the change is achieved.

**The sign convention on work:** the work done by the system is negative while the work done on the system is positive.

translational, electronic, vibrational, rotational, and nuclear or any other types of energy all contribute to the internal energy of the system. Further, you must note that not all systems will have all the types of energies mentioned above. For example, a system containing certain amount of a monoatomic gas would not have vibrational energy. Can you think why? It is so because for the vibration motion to be executed there must be at least two bonded atoms (a diatomic molecule).

As there are no means of measuring or knowing all these energies for a given system, the absolute value of the internal energy of any system cannot be known but every system has some value of its internal energy,  $U$ . However the change in internal energy  $\Delta U$  is measurable. It refers to the change in internal energy when a system changes from an initial state having an internal energy  $U_i$  to a final state of internal energy  $U_f$ ,

$$\Delta U = U_f - U_i \quad \dots (2.1)$$

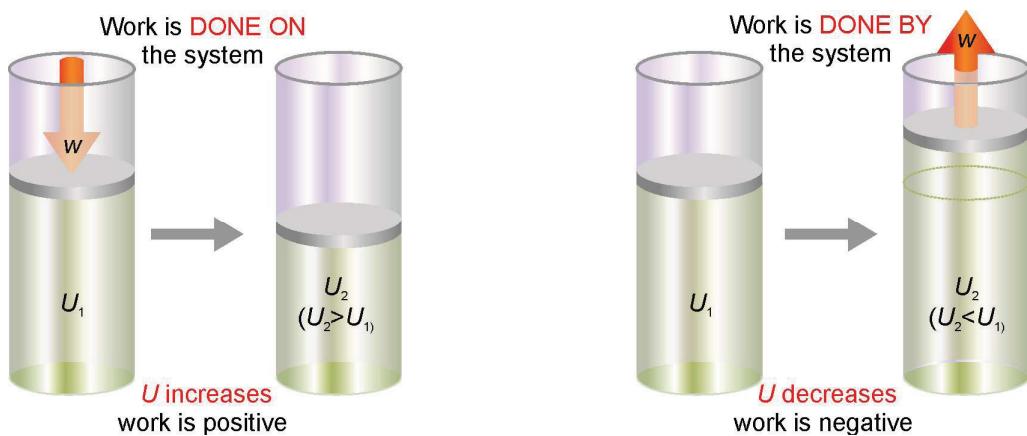
Let us try to have an insight into internal energy by taking an adiabatic system (that does not allow any exchange of heat with the surrounding) in some state (say state 1) having a value of internal energy  $U_1$  and do some work on it. This would lead to a change in state of the system and the system now would be in a new state (say state 2) having an internal energy  $U_2$ . As work is also a kind of energy the new internal energy  $U_2$  would be higher than  $U_1$ . Since there is no other energy input, we can write,

$$\Delta U = U_2 - U_1 = w_{\text{adiabatic}} \quad \dots (2.2)$$

The added energy in the form of work would increase the kinetic energy of the molecules of the system and the temperature would increase. On the other hand, if the same adiabatic system in state with internal energy  $U_1$  does some work on the surroundings it would be at the expense of its internal energy. The final value of internal energy,  $U_2$  will be smaller than  $U_1$ ; the work would become negative.

$$\Delta U = U_2 - U_1 = -w_{\text{adiabatic}} \quad \dots (2.3)$$

A schematic representation of the sign convention on work in the context of thermodynamics is given in Fig. 2.1.



**Fig. 2.1: A schematic representation of the sign convention on work.**

Let us once again take the same system in same state having internal energy  $U_1$  and perform another experiment. In this experiment we change the walls of the system such that the heat can be transferred to the system from the surroundings and also design the experiment in such a way that there is no work done on the system or by the system. Now let us transfer certain amount of heat from the surrounding to the system such that the system has same change in temperature as before. In other words the system comes to same state characterised by the internal energy  $U_2 > U_1$ ; in such a case we can write,

$$\Delta U = U_2 - U_1 = q \text{ (no work; } w=0) \quad \dots (2.4)$$

Similarly, if the system lost heat to the surroundings under similar conditions, it would be at the expense of its internal energy and the value of  $U_2$  will be smaller than  $U_1$ ; the  $q$  would become negative.

$$\Delta U = U_2 - U_1 = -q \text{ (no work; } w=0) \quad \dots (2.5)$$

A schematic representation of the sign convention on heat in the context of thermodynamics is given in Fig. 2.2.

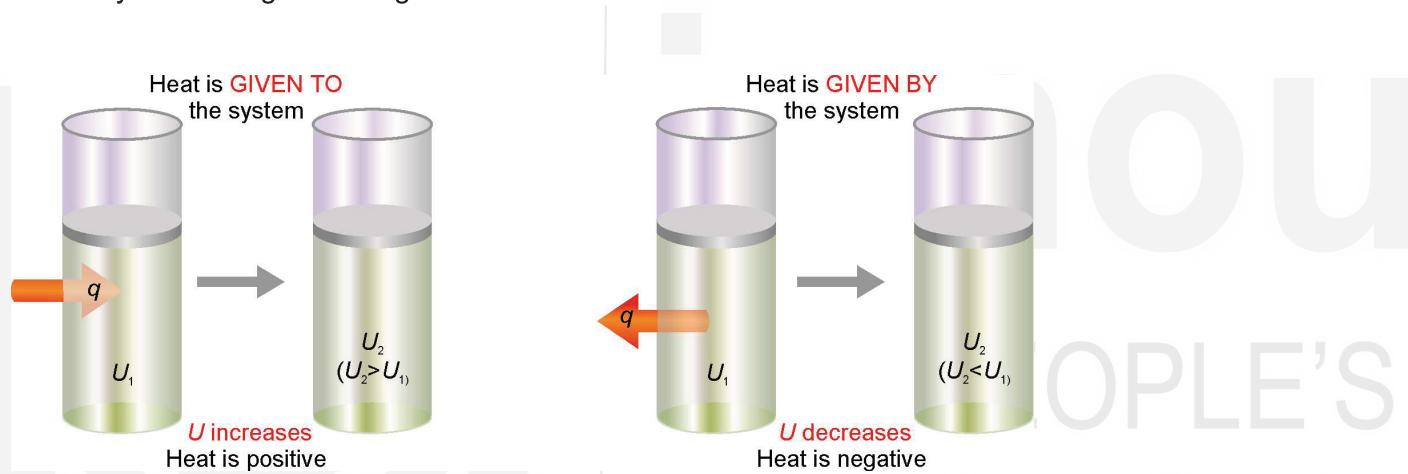
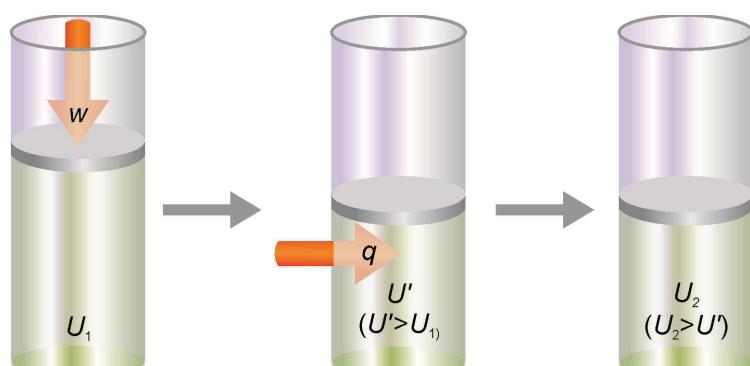


Fig. 2.2: A schematic representation of the sign convention on heat.

Going further, we may design a yet another experiment wherein we allow the transfer of certain amount of heat to the system and also perform some work on it adiabatically such that the system has same change in temperature as before. In other words the system comes to same state characterised by the internal energy  $U_2$ .

#### The sign convention on heat

The heat given to the system is positive while the heat given by the system to the surroundings is negative.



Anything (heat or work) that increases the internal energy of the system is positive and the one that decreases the internal energy of the system is negative

Fig. 2.3: A schematic representation showing effect of work and heat on internal energy.

The way we have defined internal energy here amounts to saying that the internal energy is a state function; the one which depend only on the state of the system and not on how that state has been achieved.

In such a case we can write,

$$\Delta U = U_2 - U_1 = q + w \quad \dots (2.6)$$

This leads us to the IUPAC definition of internal energy.

*IUPAC defines internal energy as the quantity, the change in which is equal to the sum of heat,  $q$ , brought to the system and work,  $w$ , done on it,  $\Delta U = q + w$ .*

### State and Path Functions

You may have noticed that we have used different types of symbols for three quantities used above, namely heat,  $q$ , work,  $w$  and internal energy,  $U$ . For internal energy we used a capital letter whereas for heat and work we have used lower case letters. This has been done to convey the fact that while internal energy is a state function, heat and work are path functions. A '**state function**' is a property of the system that depends only on the current state of the system and is independent of the way the state is achieved.

To understand the difference between a state function and a path function, let us take a thermodynamic system in state 1 having the internal energy as  $U_1$  and transfer  $q$  amount of heat to it such that the system is now at state 2 with internal energy  $U_2$ . You would recall from the above, that the system with  $U_1$  could also be taken to  $U_2$  by doing work on it. Thus, we find that in the first case the change from state 1 to state 2 was associated with  $q$  amount of heat energy and no work whereas in the second case there was  $w$  work and no associated heat change.

We may take up another case where we start with the same system at state 1 and transfer  $q'$  ( $q' < q$ ) amount of heat to it; the system will reach some state (state 1') different from state 2 and then we do sufficient work on the system so as to make it reach state 2. In this case, the change in state ( $1 \rightarrow 2$ ) is associated with heat and work changes. We may take up a yet another case where we initially do some work on the system ( $w' < w$ ) and then supply sufficient amount of heat to it to make it reach, state 2. The four cases are schematically given in Fig.2.4.

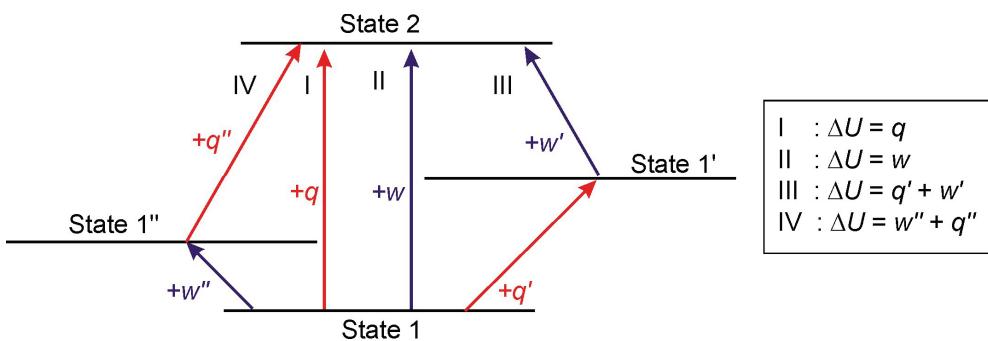


Fig. 2.4: A schematic diagram showing that work and heat are path functions.

You may note that in all the four cases taken here we go from state 1 ( $U_1$ ) to state 2 ( $U_2$ ) i.e., the change in internal energy is same but the amount of work done or the associated heat change is different in all the cases. In other words, the internal energy depends on the state of the system i.e., it is a **state function** whereas heat and work *depend on the path* taken for going from state 1 to state 2. Heat and work are accordingly called **path functions**.

Having learnt about the concept of internal energy we are now equipped to learn about the first law of thermodynamics.

## 2.2.2 The First Law of Thermodynamics and Internal Energy

You have learnt about the first law of thermodynamics in your earlier classes as the law of conservation of energy i.e., *energy can neither be created nor be destroyed although it can be changed from one form to another*. You may also have come across many other statements for the First law of thermodynamics. Some of these are

Die Energie der Welt  
ist Konstant  
-Clausius, 1867

- The total energy of universe is constant.
- It is not possible to construct a machine showing perpetual motion of the first kind. That is, a machine, which can work endlessly without the expenditure of energy.
- The internal energy of an isolated system is constant;  $\Delta U_{\text{sys (isolated)}} = 0$

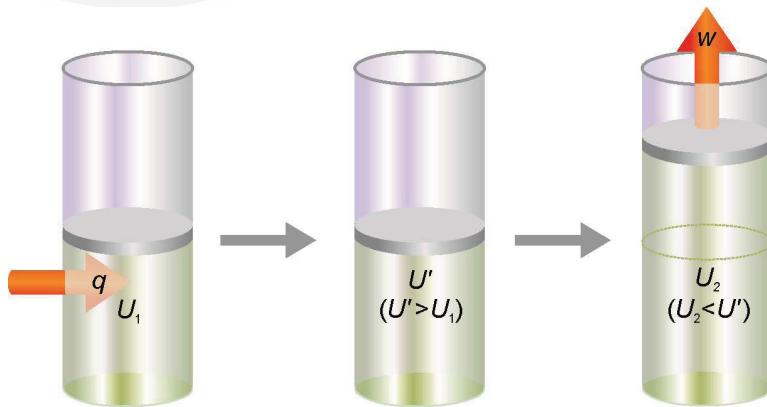
These statements are alternative expressions for the principle of conservation of energy.

### Mathematical Expression of the First Law of Thermodynamics

The definition of first law in terms of  $\Delta U_{\text{sys (isolated)}} = 0$  is not of wider applications as most of the systems we come across or work with are either open or closed systems. In such cases, the exchange of matter or energy between the system and the surroundings is allowed. Moreso, we are particularly interested in the energy changes of the system. Let us take up certain situations that we may come across.

There is no proof for first law of thermodynamics; the absence of any contradiction to it makes us believe in it.

**Case I:** We transfer  $q$  amount of heat ( $+q$ ) to a system having internal energy,  $U_1$ , that increases its internal energy to  $U'$  and the system in turn does certain work on the surroundings ( $-w$ ) leading to decrease in the internal energy to  $U_2$ .

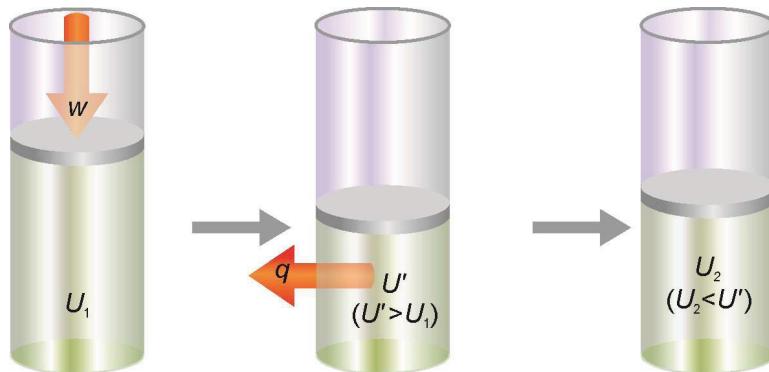


In such a case where the heat supplied to the system has caused some change in the internal energy and produced some work, we can write the following expression,

$$q = \Delta U + (-w) \quad \dots (2.7)$$

This can be rearranged to get Eq. (2.6);  $\Delta U = q + w$

**Case II:** We do certain amount of work ( $+w$ ) on the system having internal energy,  $U_1$ , that increases its internal energy to  $U'$  and the system in turn transfers  $q$  amount of heat to the surroundings ( $-q$ ) leading to decrease in the internal energy to  $U_2$ .

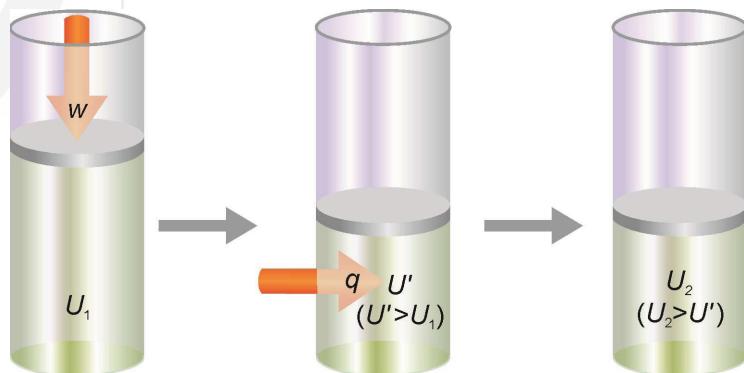


In such a case where the work done on the system has caused some change in the internal energy and produced some heat in the surrounding, we can write the following expression,

$$w = \Delta U + (-q) \quad \dots (2.8)$$

This again can be rearranged to Eq. (2.6);  $\Delta U = q + w$

**Case III:** The third possibility is that we do certain amount of work ( $+w$ ) on the system having internal energy,  $U_1$ , that increases its internal energy to  $U'$  and also transfer certain amount of heat ( $+q$ ) to the system which increase the internal energy to  $U_2$ .



In such a case where the heat supplied to the system and the work done on the system cause change in the internal energy, we can write the following expression,

$$\Delta U = q + w \quad \dots (2.9)$$

Which is same as Eq. (2.6). We find that in all the three cases we get the identical expression for the change in the internal energy of the system. *This is the mathematical expressions for the first law of thermodynamics.* You must keep in mind that in this expression the  $q$  and  $w$  are inclusive of their signs. Let us take up a simple example to see the application of the mathematical expression for the first law of thermodynamics.

**Example 2.1:** 380 J of heat was supplied to a thermodynamic system and its internal energy decreased by 72 J. Was any work destroyed in the surroundings?

**Solution:** As per the Eq. (2.6), we can write,

$$\Delta U = q + w$$

If the surroundings do some work on the system we say that the work is destroyed in the surroundings.

The amount of energy supplied to the system as heat,  $q = 380 \text{ J}$

The change in the internal energy,  $\Delta U = -72 \text{ J}$

Substituting in the Eq. (2.6) we get,  $-72 \text{ J} = 380 \text{ J} + w$

Solving we get,

$$w = -452 \text{ J}$$

- ⇒ The work comes out to be negative implying that the **system** has done work on the surroundings. Thus, no work was destroyed in the surroundings.

For infinitesimal (very small) changes in state in which a small amount of heat  $dq$  is added to the system, the system does a small amount of work  $-dw$ , and its internal energy changes by an amount  $dU$  we can write,

$$dU = dq + (-dw) \quad \dots (2.10)$$

$dq$  and  $dw$  are often written as  $\partial q$  and  $\partial w$  or as  $dq$  and  $dw$  so as to emphasise the fact that these are inexact differentials as these depend on the path.

Now, suppose a system goes from state 1 to state 2 in a number of small steps each associated with an infinitesimal change in heat, work and internal energy ( $dq$ ,  $dw$  and  $dU$  respectively), the overall changes for the process can be obtained by integrating the step wise changes. When we do so the following results are obtained,

$$\int dw = w \quad \dots (2.11)$$

$$\int dq = q \quad \dots (2.12)$$

$$\int dU = \Delta U \quad \dots (2.13)$$

That is, when  $dw$  and  $dq$  are integrated, the result is the absolute amount of work,  $w$  and heat,  $q$  respectively for the process, however when  $dU$  is integrated, the result is not the absolute value of internal energy,  $U$  but the change in it i.e.,  $\Delta U$ , for the process. This is an important consequence of the fact that the internal energy is a state function whereas heat and work are path functions. Please answer the following self assessment question to assess your understanding of the first law of thermodynamics.

### SAQ 1

416 J of heat was supplied to a system and its internal energy was found to have increased by 268 J. Was any work associated with the system? Determine the type and magnitude of the work involved.

## 2.3 HEAT CHANGES AT CONSTANT VOLUME

The heat change accompanying a process can be measured in terms of the change in the temperature of the system. The heat change in such a case would equal the product of the mass (m) of the system, its heat capacity (C) and the change in temperature  $\Delta T$  i.e.,

$$q = m \times C \times \Delta T \quad \dots (2.14)$$

This equation is valid for systems of any size, however, we generally deal with systems having 1 mole of the substance and the heat capacity as  $\bar{C}_v$ , molar heat capacity, which is an intensive property and has the units of  $\text{JK}^{-1}\text{mol}^{-1}$ .

A process occurring under the conditions of constant volume can be represented as:

$$\text{State 1 } (V_1, T_1) \rightarrow \text{State 2 } (V_1, T_2)$$

And the heat change accompanying it can be given as:

$$q_v \quad \text{or} \quad dq_v \text{ (for infinitesimal change)}$$

We know that as per the First Law of thermodynamics, we have

$$dU = dq + dw \quad \dots (2.15)$$

under the conditions of constant volume, the term,  $dw$  is equal to zero and we can write,

$$dU = dq_v \quad \dots (2.16)$$

This implies that *all the heat supplied to the system at constant volume goes to increase its internal energy.*

Once again, from the first law of thermodynamics, we can write

$$dq_v = dU + pdV \quad \dots (2.17)$$

Where  $p\Delta V$  is the work involved in the process. Dividing both sides by  $dT$  we get,

$$\frac{dq_v}{dT} = \frac{dU + pdV}{dT} \quad \dots (2.18)$$

At constant volume,  $dV = 0$ , i.e., there is no work of expansion, so we get

$$\left( \frac{dq_v}{dT} \right)_V = \left( \frac{dU}{dT} \right)_V \quad \dots (2.19)$$

The term on the left hand side of Eq. (2.19) is the heat capacity at constant volume therefore we can write,

$$C_v = \left( \frac{dU}{dT} \right)_V \quad \dots (2.20)$$

The subscript, v specifies that the volume is constant for the system. This equation *relates the rate of change of internal energy of the system with temperature under conditions of constant volume with the heat capacity-a measurable quantity.* Rearranging Eq. (2.20), we get

$$dU = C_v dT \quad \dots (2.21)$$

We can integrate this equation for infinitesimal changes to obtain the change in internal energy for a finite change in temperature at constant volume.

$$\Delta U_V = \int_{T_1}^{T_2} C_V dT \quad \dots(2.22)$$

For a small range of temperature, the heat capacity at constant volume is constant therefore we can take  $C_V$  out of the integral symbol and write,

$$\Delta U_V = C_V \int_{T_1}^{T_2} dT \quad \dots(2.23)$$

Integrating and applying limits

$$\Delta U_V = C_V [T]_{T_1}^{T_2} \quad \dots(2.24)$$

$$\Delta U_V = C_V [T_2 - T_1] = C_V \Delta T \quad \dots(2.25)$$

We showed above, that  $\Delta U_V = q_V$ , Eq. (2.16) therefore we can write,

$$q_V = C_V \Delta T \quad \dots(2.26)$$

$$\Rightarrow C_V = \frac{q_V}{\Delta T} \quad \dots(2.27)$$

This relation forms the basis for a simple method for the measurement of the heat capacity of a sample. In this method we transfer a measured quantity of energy as heat to the sample and note the change (increase) in the temperature of the system. The data is then used to compute the heat capacity of the sample under constant volume conditions. Let us take an example to understand it better.

**Example 2.2 :** A certain amount an organic compound was combusted in a bomb calorimeter of fixed volume having a heat capacity of  $3.80 \text{ kJ K}^{-1}$ . The temperature of the calorimeter increased from  $22.70^\circ\text{C}$  to  $26.10^\circ\text{C}$ . Calculate the amount of heat generated by the reaction.

You would learn about bomb calorimetry in Unit 3

**Solution:** As the reaction has occurred under the conditions of constant volume, we need to find  $q_V$  and as per Eq. (2.26),  $q_V = C_V \Delta T$

Given:  $C_V = 3.80 \text{ kJ K}^{-1}$  and  $\Delta T = (26.10 - 22.70) = 3.40^\circ\text{C} = 3.40 \text{ K}$

Substituting in the expression for  $q_V$ ,

$$q_V = 3.80 \text{ kJ K}^{-1} \times 3.40 \text{ K} = 12.92 \text{ kJ}$$

⇒ Thus, the amount of heat generated by the reaction =  $12.92 \text{ kJ}$

In the next unit you would be learning in details about such experiments on Calorimetry.

Let us now take up the heat changes accompanying the thermodynamic processes occurring under the conditions of constant pressure.

The heat capacity of most substances does not change much over short ranges of temperature.

## 2.4 HEAT CHANGES AT CONSTANT PRESSURE: ENTHALPY

Thus, in the process of relating the heat changes accompanying a process occurring under the conditions of constant pressure we have got a new thermodynamic property, enthalpy, H.

You may note here that as we cannot know the absolute value of internal energy of a system we cannot know its absolute enthalpy also. We can only measure the change in enthalpy and fortunately, for most of the processes we only need the changes in enthalpy.

If the pV work is the only kind of work, then the heat change accompanying a reaction in a constant-pressure calorimeter can be visualised as a measure of the decrease in enthalpy of the system.

We had shown above that the heat transferred to a system under the conditions of constant volume (i.e., when there is no work of expansion) goes to increase the internal energy of the system. However, most of the chemical reactions are carried out under the conditions of atmospheric pressure or in other words at constant pressure. In such a situation, the system can change the volume i.e., it may expand. In such a process part of the energy given to the system goes back to the surroundings as work of expansion. This implies that a part of the energy supplied as heat at constant pressure,  $q_p$ , goes to increase the internal energy and rest comes back to the surroundings as  $p\Delta V$ . We can, therefore, write,

$$q_p = \Delta U_p + p \Delta V \quad \dots(2.28)$$

$$\Delta U_p = q_p - p \Delta V \quad \dots(2.29)$$

The thermodynamic process (state 1 → state 2) occurring under the conditions of constant pressure can be represented as

$$(p, V_1, T_1) \rightarrow (p, V_2, T_2)$$

The corresponding values of the internal energy would be  $U_1$  and  $U_2$  respectively; the Eq. (2.29) can be rewritten as

$$U_2 - U_1 = q_p - p(V_2 - V_1) \quad \dots(2.30)$$

The equation can be rearranged to

$$q_p = [U_2 + pV_2] - [U_1 + pV_1] \quad \dots(2.31)$$

The terms given in the brackets of Eq. (2.31) consist of combination of state functions ( $U$ ,  $p$  and  $V$ ) therefore this combination also represents a state function. This new state function is called **enthalpy**, denoted as  $H$ , and is defined as

$$H = U + pV \quad \dots(2.32)$$

The Eq. (2.31) can then be rewritten as

$$q_p = H_2 - H_1 = \Delta H \quad \dots(2.33)$$

This implies that *the heat withdrawn from the surroundings in a process at constant pressure is equal to the change in enthalpy of the system if only work involved is pressure-volume work.*

For an infinitesimal change, we can write,

$$dq_p = dH \quad \dots(2.34)$$

From first law of thermodynamics we can write,

$$dq = dU + p dV \quad \dots(2.17)$$

Dividing both sides by  $dT$  we get,

$$\frac{dq}{dT} = \frac{dU + pdV}{dT} \quad \dots(2.35)$$

At constant pressure, we get

$$\left(\frac{dq}{dT}\right)_p = \left(\frac{dU}{dT}\right)_p + p\left(\frac{dV}{dT}\right)_p \quad \dots(2.36)$$

We defined enthalpy as,  $H = U + pV$

Differentiating it with respect to  $T$  at constant pressure we get,

$$\left(\frac{dH}{dT}\right)_p = \left(\frac{dU}{dT}\right)_p + p\left(\frac{dV}{dT}\right)_p \quad \dots(2.37)$$

Equating Eq.(2.36) and Eq.(2.37) we get,

$$\left(\frac{dq}{dT}\right)_p = \left(\frac{dH}{dT}\right)_p \quad \dots(2.38)$$

As mentioned above, generally the heat changes accompanying a chemical reaction are measured under the conditions of constant pressure i.e., we get the change in the enthalpy of the reaction. This can then be used to compute the change in internal energy with the help of the following equation.

$$\Delta U = \Delta H - P\Delta V$$

The expression on the left hand side represents,  $C_p$ , heat capacity at constant pressure, we can write,

$$C_p = \left(\frac{dH}{dT}\right)_p \quad \dots(2.39)$$

The subscript,  $p$  specifies that the pressure in the process is constant. This equation relates the rate of change of enthalpy of the system with temperature under conditions of constant pressure with the heat capacity-a measurable quantity.

Rearranging the equation, we can write,

$$dH = C_p dT \quad \dots(2.40)$$

We can integrate this equation for infinitesimal change to obtain the change in enthalpy for a finite change in temperature at constant pressure.

$$\Delta H = \int_{T_1}^{T_2} C_p dT \quad \dots(2.41)$$

For a small range of temperature, the heat capacity at constant pressure is constant therefore take  $C_p$  out of the integral symbol and write,

$$\Delta H = C_p \int_{T_1}^{T_2} dT \quad \dots(2.42)$$

Integrating,

$$\Delta H = C_p [T]_{T_1}^{T_2} \quad \dots(2.43)$$

$$\Delta H = C_p [T_2 - T_1] = C_p \Delta T \quad \dots(2.44)$$

This equation is valid for systems of any size, however, we generally deal with systems having 1 mole of the substance and the heat capacity as  $C_p$ , molar heat capacity, which is an intensive property and has the units of  $\text{JK}^{-1}\text{mol}^{-1}$ .

The heat capacity of most substances does not change much over short ranges of temperature.

As an increase in enthalpy can be equated with the energy supplied as heat under the conditions of constant pressure, we can write,

$$\Delta H = q_p = C_p \Delta T \quad \dots(2.45)$$

This expression (Eq. 2.45) provides us a method to measure the heat capacity of a sample. For this we supply a measured quantity of energy as heat to the system under conditions of constant pressure and measure the rise in temperature. Having learnt about the heat changes under the conditions of constant volume and constant pressure respectively and relating them to the state functions, let us now try to establish the relationship between two types of heat capacities.

### Relationship between $C_p$ and $C_V$

We know that,  $C_p = \left(\frac{dH}{dT}\right)_p$  and  $C_V = \left(\frac{dU}{dT}\right)_V$

$$\text{Also, } H = U + pV \quad \dots(2.32)$$

$$\text{For 1 mole of an ideal gas } pV = RT$$

$$\rightarrow H = U + RT \quad \dots(2.46)$$

Differentiating the expression w.r.t.  $T$  we get,

$$\left(\frac{dH}{dT}\right) = \left(\frac{dU}{dT}\right) + R \quad \dots(2.47)$$

$$\rightarrow C_p = C_V + R \quad \dots(2.48)$$

$$\rightarrow C_p - C_V = R \quad \dots(2.49)$$

Therefore, for ideal gas the value of  $C_p$  is greater than  $C_V$  by  $R$ , the gas constant. You have so far learnt about the first law of thermodynamics, its significance and two very important state functions viz., internal energy and enthalpy. Let us now try to apply the first law to understand the behaviour of gases. We would be taking up the calculation of the work for the gases undergoing expansion under isothermal and adiabatic conditions. We begin with the isothermal expansion of gases. However, before moving ahead solve the following self assessment questions.

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### SAQ 2

Define enthalpy and give its significance.

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### SAQ 3

Calculate the amount of heat required to increase the temperature of 1.00 mole of argon from a temperature of 100 K to 900 K in

- a) an isobaric process and
- b) in a isochoric process.

(Given:  $C_{V,m} = 12.47 \text{ J K}^{-1}\text{mol}^{-1}$  and  $C_{p,m} = 20.78 \text{ J K}^{-1}\text{mol}^{-1}$ )

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## 2.5 WORK OF EXPANSION

You know that the gases expand if the external pressure on them is lower than their own pressure. As the system alters its volume against an opposing pressure, it produces work in the surroundings; we say the system has done work. If however, the external pressure is more than the gas pressure the surroundings would perform work on the system and its volume would decrease, the process would be called **compression**. We would focus our attention on the work associated with the expansion of gases under isothermal and adiabatic conditions.

### 2.5.1 Isothermal Expansion

You have learnt in Unit 1 that an isothermal process is the one in which there is no change in the temperature of the system. You have also learnt that the thermodynamic processes could be reversible or irreversible depending on how do we perform it. It is advisable that you revisit Section 1.5 of Unit 1 where we have discussed about reversible and irreversible thermodynamic processes. Here, we would derive expressions for work obtained respectively in irreversible and reversible isothermal expansion of an ideal gas.

#### Irreversible Isothermal Expansion

Let us take a thermodynamic system consisting of a sample of ideal gas contained in a cylinder fitted with frictionless and massless piston of a cross-section area  $A \text{ m}^2$ ; and a mass of 1 kg is placed on the piston. Since we wish to perform the expansion under isothermal conditions, we immerse the cylinder in a thermostat to keep the temperature of the system constant throughout the process, Fig. 2.5 (a). The gas occupies a volume  $V_1$  at an initial pressure equal to the atmospheric pressure and the pressure exerted by the mass on the piston; we call this pressure  $p_1$ . The thermodynamic state of the system would be given as  $(p_1, V_1, T)$ .

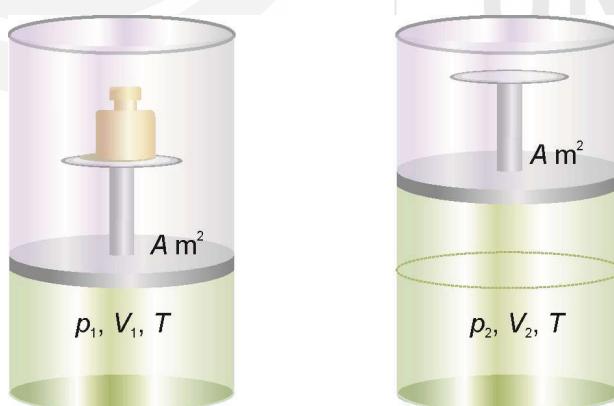


Fig. 2.5: Experimental design for isothermal irreversible expansion of a gas.

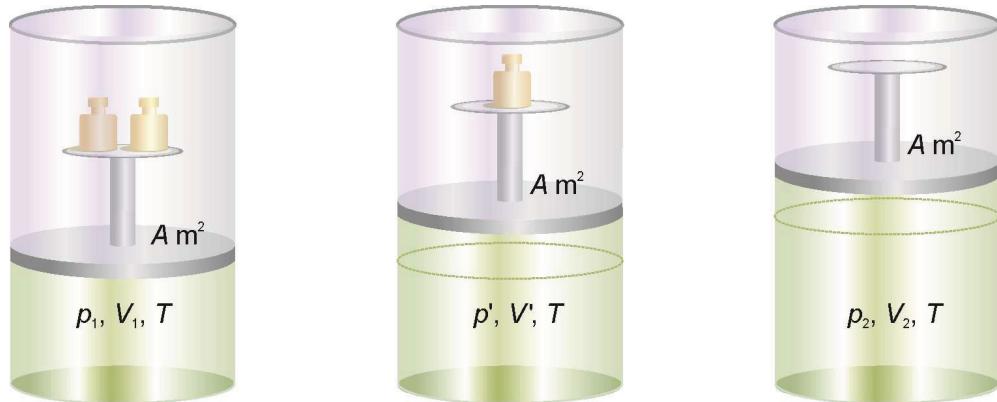
Let's now remove the 1 kg mass from the piston; the pressure reduces and becomes equal to the atmospheric pressure; let's call it  $p_2$ . The gas would expand to volume  $V_2$  against the opposing pressure  $p_2$ , the new state of the system would be  $(p_2, V_2, T)$ . The expansion of the gas would produce work in the surroundings (work is done by the system) and is given as

$$\text{Work} = w_1 = -p_2(V_2 - V_1) \quad \dots(2.50)$$

This is the expression if the irreversible expansion happens in a single step. Let's ask if we perform the same expansion in two steps, what would be the work? Let's see!

### Irreversible Isothermal Expansion in Two Steps

Let us take the same system again at state-1( $p_1, V_1, T$ ) however, we place the mass of 1 kg in terms of two masses of 500 g each as shown in Fig. (2.6).



**Fig. 2.6: Experimental design for isothermal irreversible expansion of a gas in a two-step process.**

Let's now remove one of the 500 g masses from the piston; the pressure reduces to be equal to the atmospheric pressure plus that exerted by the 500 g mass; let's call it  $p'$ . The gas would expand to volume  $V'$  against the opposing pressure  $p'$  the new state of the system would be  $(p', V', T)$ . The expansion of the gas would produce work in the surroundings and is given as

$$w' = -p'(V' - V_1) \quad \dots(2.51)$$

Now when we remove the second 500 g mass from the piston; the pressure reduces to be equal to the atmospheric pressure; let's again call it  $p_2$ . The gas would expand to volume  $V_2$  against the opposing pressure  $p_2$ ; the new state of the system would be  $(p_2, V_2, T)$ . The expansion of the gas would again produce work in the surroundings and is given as

$$w'' = -p_2(V_2 - V') \quad \dots(2.52)$$

The total work done by the system would be

$$w' + w'' = -p'(V' - V_1) + [-p_2(V_2 - V')] \quad \dots(2.53)$$

This work would be more than that obtained in the single step process. Can you think how? It is so because in the single step process the expansion was against pressure  $p_2$  whereas in the two step process about half of the expansion was against the pressure  $p_2$  and the rest was against a pressure  $p'$  which is greater than  $p_2$ . You may note that the overall change in the volume is same as in single step process.

### Reversible Isothermal Expansion

You would recall from section 1.4 that a thermodynamic reversible process is the one, which occurs, in an infinite number of infinitesimally small steps. Let

us workout an expression for the work done in a reversible expansion occurring under isothermal conditions. In order to do so we need to design a yet another experiment; we take the same system at state  $(p_1, V_1, T)$  as before and perform the expansion to volume  $V_2$  in such a way that we slowly vary the opposing pressure created by the mass on the piston. We start with the external pressure, to be infinitesimally smaller than the pressure  $p_1$  of the gas i.e.,  $(p_1 - dp)$ . The gas expands to a volume  $(V_1 + dV_1)$  while the temperature remains  $T$ . The process for the first step of the expansion can be given as

$$(p_1, V_1, T) \rightarrow (p_1 - dp, V_1 + dV_1, T)$$

The infinitesimal amount of work obtained would be

$$= dw' = -(p_1 - dp)(V_1 + dV_1 - V_1) \quad \dots(2.54)$$

$$\Rightarrow - (p_1 - dp) dV_1 \quad \dots(2.55)$$

Once the equilibrium is achieved after expansion, we decrease the pressure infinitesimally again to let the gas expand to volume  $V''$  and continue doing the same till the volume of the gas becomes  $V_2$ . Expressions similar to Eq. (2.55) would represent work done by the system in each successive step. The generalised expression for the work done by the system in an infinitesimal expansion can be given as follows.

$$dw = -(p - dp) dV \quad \dots(2.56)$$

For a large number of steps, the work obtained from each step can be added to get the overall work.

$$w = \sum dw = \sum [-(p - dp) dV] \quad \dots(2.57)$$

As each successive step happens to be infinitesimally small and number of steps is infinite, we can replace summation by integral and the expression for work becomes,

$$w = \int_{V_1}^{V_2} dw = - \int_{V_1}^{V_2} (p - dp) dV \quad \dots(2.58)$$

$$w = - \int_{V_1}^{V_2} (pdV - dpdV) \quad \dots(2.59)$$

Where,  $V_1$  and  $V_2$  are the initial and final volumes. Further, the second term in the bracket is much smaller than the first term and can be ignored. We get,

$$w = - \int_{V_1}^{V_2} (pdV) \quad \dots(2.60)$$

Since this work is obtained in an infinite number of steps we call this work to be the maximum possible work that can be obtained from an expansion process. We can then write,

$$w_{\max} = - \int_{V_1}^{V_2} (pdV) \quad \dots(2.61)$$

We have shown that the work done by the system in two steps is more than that obtained in the same expansion performed in a single step. We can extend the argument and show that more the number of steps more the work. For infinite number of steps the work is maximum.

What we have just obtained is an expression for computing the maximum possible work of expansion for a given sample of gas. Let us get a little more specific and formulate the expression for the expansion of a sample of an ideal gas occurring at a constant temperature (isothermally).

We know from the ideal gas equation that for  $n$  moles of an ideal gas, at a temperature  $T$ , the pressure can be given as

$$p = \frac{nRT}{V} \quad \dots(2.62)$$

Substituting in the Eq. (2.61) we get,

$$w_{\max} = - \int_{V_1}^{V_2} \frac{nRT}{V} dV \quad \dots(2.63)$$

On simplifying, at constant temperature

$$w_{\max} = -nRT \int_{V_1}^{V_2} \frac{dV}{V} \quad \dots(2.64)$$

Integrating and applying limits, we get,

$$w_{\max} = -nRT \ln \frac{V_2}{V_1} \quad \dots(2.65)$$

$$w_{\max} = -2.303nRT \log \frac{V_2}{V_1} \quad \dots(2.66)$$

We know that for 1 mole of an ideal gas

$$p_1 V_1 = p_2 V_2 \Rightarrow \frac{V_2}{V_1} = \frac{p_1}{p_2} \quad \dots(2.67)$$

Substituting in Eq. (2.66), we get,

$$w_{\max} = -2.303nRT \log \frac{p_1}{p_2} \quad \dots(2.68)$$

The equations 2.66 and 2.68 are important expressions that can be used to compute the maximum amount of work that can be obtained from the isothermal expansion of an ideal gas. Let us take an example to see their applicability.

**Example 2.3:** 0.40 moles of argon behaving as an ideal gas is made to expand from a volume of  $7.50 \text{ dm}^3$  to  $11.25 \text{ dm}^3$  at  $27^\circ\text{C}$ . What is the maximum work that can be obtained from this expansion?

**Solution:** As per the Eq. (2.66), the maximum work of expansion of an ideal gas is given as

$$w_{\max} = -2.303nRT \log \frac{V_2}{V_1}$$

The data given is as under:

$$n = 0.4 \text{ mol} \quad V_1 = 7.50 \text{ dm}^3 \quad V_2 = 11.25 \text{ dm}^3$$

$$T = 273.15 + 27 = 300.15 \text{ K}$$

Substituting the values in the expression, we get

$$w_{\max} = -2.303 \times 0.40 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 300.15 \text{ K} \times \log \frac{11.25}{7.5} = -404.82 \text{ J}$$

⇒ Thus a maximum work equal to 404.82 J can be done by the system on the surroundings

Having learnt about the isothermal expansion of ideal gases under different conditions let us take up adiabatic expansion, however before that answer the following simple question to gauge your understanding and applications of these expressions.

#### *SAQ 4*

One mole of an ideal gas at 25°C is allowed to expand reversibly at constant temperature from a volume of 10 dm<sup>3</sup> to 20 dm<sup>3</sup>. Calculate the work done by the gas.

### 2.5.2 Adiabatic Expansion

As you know, an adiabatic process is the one in which no heat can either enter or leave the system. As  $dq=0$ , the first law expression for such a case can be written as

$$dU = dw_{\text{adi.}} \quad \dots (2.69)$$

For a sample of a gas at pressure  $p$  and a volume  $V$ , if there is an infinitesimal increase in the volume  $dV$  at pressure  $p$ , the work done by the gas would be  $-pdV$  and the corresponding decrease in the internal energy would be  $dU$ . If the work happens to be only the work of expansion the expression becomes

$$dU = -pdV \quad \dots (2.70)$$

If the system expands adiabatically,  $dV$  is positive and therefore,  $dU$  is negative. This implies that as no energy enters the system as heat, the work done in the adiabatic process is at the expense of the internal energy. The decrease in internal energy means that the kinetic energy of the molecules fall, i.e., their average speed decreases, and hence the temperature falls. The relationship applies to any adiabatic process, reversible or irreversible, if only work of expansion is involved.

Thus, we can say qualitatively that a change in the volume of a gas against a non-zero opposing pressure, under adiabatic conditions causes change in its temperature. The question arises how are the temperature and volume related for an adiabatic expansion? How can we calculate the change in the temperature of the system? In order to do so we need to establish a relationship between the temperature and volume of the system for an adiabatic process.

### Relationship between the Temperature and Volume for an Adiabatic Process

Let us work out the relationship between the temperature and volume for an adiabatic process.

$$\text{We know that } dU = C_V dT \quad \dots(2.21)$$

Equating the Eq. (2.70) and (2.21) we can write

$$C_V dT = -p dV \quad \dots(2.71)$$

For an ideal gas we can write,  $p = nRT/V$ , we get

$$C_V dT = -\frac{nRT}{V} dV \quad \dots(2.72)$$

Rearranging,

$$\frac{C_V dT}{T} = -\frac{nR dV}{V} \quad \dots(2.73)$$

For the adiabatic change  $[(V_1, T_1) \rightarrow (V_2, T_2)]$ , and assuming that  $C_V$  is constant for the range of temperature we can integrate Eq. (2.67) to get,

$$C_V \int_{T_1}^{T_2} \frac{dT}{T} = -nR \int_{V_1}^{V_2} \frac{dV}{V} \quad \dots(2.74)$$

$$C_V \ln \frac{T_2}{T_1} = -nR \ln \frac{V_2}{V_1} \quad \dots(2.75)$$

On rearranging,

$$\frac{C_V}{nR} \ln \frac{T_2}{T_1} = -\ln \frac{V_2}{V_1} = \ln \frac{V_1}{V_2} \quad \dots(2.76)$$

Using the property of logarithm, we get

$$\ln \left( \frac{T_2}{T_1} \right)^{\frac{C_V}{nR}} = \ln \frac{V_1}{V_2} \quad \dots(2.77)$$

Taking antilogarithms on both the sides

$$\left( \frac{T_2}{T_1} \right)^{\frac{C_V}{nR}} = \frac{V_1}{V_2} \quad \dots(2.78)$$

$$\Rightarrow \frac{T_2}{T_1} = \left( \frac{V_1}{V_2} \right)^{\frac{nR}{C_V}} \quad \dots(2.79)$$

Substituting  $n = 1$  and  $R = C_p - C_V$ ; we get,

$$\Rightarrow \frac{T_2}{T_1} = \left( \frac{V_1}{V_2} \right)^{\frac{C_p - C_V}{C_V}} \quad \dots(2.80)$$

$$\Rightarrow \frac{T_2}{T_1} = \left( \frac{V_1}{V_2} \right)^{\gamma-1} \quad \dots(2.81)$$

where,  $\gamma = \frac{C_p}{C_v}$

Rearranging, we get

$$\Rightarrow T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1} \text{ or } T V^{\gamma-1} = \text{constant} \quad \dots(2.82)$$

This gives the relationship between volume and temperature for a reversible adiabatic process.

### Relationship between the Temperature and Pressure for Adiabatic expansion

In order to get the relationship between temperature and pressure for an adiabatic expansion process we recall the ideal gas equation for 1 mol, viz.,

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2} \Rightarrow \frac{V_1}{V_2} = \frac{p_2 T_1}{p_1 T_2} \quad \dots(2.83)$$

and substitute it into the Eq. (2.81),  $\frac{T_2}{T_1} = \left( \frac{V_1}{V_2} \right)^{\gamma-1}$

$$\Rightarrow \frac{T_2}{T_1} = \left( \frac{p_2 T_1}{p_1 T_2} \right)^{\gamma-1} \quad \dots(2.84)$$

$$\Rightarrow \frac{T_2}{T_1} = \left( \frac{p_2}{p_1} \right)^{\gamma-1} \left( \frac{T_1}{T_2} \right)^{\gamma-1} \quad \dots(2.85)$$

$$\Rightarrow \frac{T_2}{T_1} \left( \frac{T_2}{T_1} \right)^{\gamma-1} = \left( \frac{p_2}{p_1} \right)^{\gamma-1} \quad \dots(2.86)$$

$$\Rightarrow \left( \frac{T_2}{T_1} \right)^\gamma = \left( \frac{p_2}{p_1} \right)^{\gamma-1} \quad \dots(2.87)$$

$$\Rightarrow \left( \frac{T_2}{T_1} \right) = \left( \frac{p_1}{p_2} \right)^{\frac{1-\gamma}{\gamma}} \quad \dots(2.88)$$

$$\Rightarrow T_1 p_1^{\frac{1-\gamma}{\gamma}} = T_2 p_2^{\frac{1-\gamma}{\gamma}} \quad \dots(2.89)$$

It is the desired equation relating temperature and pressure for an adiabatic expansion process.

### Relationship between the Pressure and Volume for Adiabatic Expansion

In order to get the relationship between the pressure and volume, we rearrange the gas equation,

$$\frac{T_2}{T_1} = \frac{p_2 V_2}{p_1 V_1} \quad \dots(2.90)$$

and substitute into the temperature-volume relationship, Eq.(2.81)

$$\begin{aligned} \frac{T_2}{T_1} &= \left(\frac{V_1}{V_2}\right)^{\gamma-1} \\ \Rightarrow \quad \left(\frac{T_2}{T_1}\right) &= \left(\frac{p_2 V_2}{p_1 V_1}\right) = \left(\frac{V_1}{V_2}\right)^{\gamma-1} \end{aligned} \quad \dots(2.91)$$

The expression can be rearranged as

$$\Rightarrow \quad \left(\frac{p_2}{p_1}\right) = \left(\frac{V_1}{V_2}\right)^{\gamma-1} \left(\frac{V_1}{V_2}\right) = \left(\frac{V_1}{V_2}\right)^{\gamma} \quad \dots(2.92)$$

$$\Rightarrow \quad \left(\frac{p_2}{p_1}\right) = \left(\frac{V_1}{V_2}\right)^{\gamma} \Rightarrow p_1 V_1^{\gamma} = p_2 V_2^{\gamma} \quad \dots(2.93)$$

It is the desired equation relating pressure and volume for an adiabatic expansion process. We can summarise the relationships between the pairs of thermodynamic properties for reversible adiabatic expansion processes as

$$\Rightarrow \quad p_1 V_1^{\gamma} = p_2 V_2^{\gamma} \quad \dots(2.93)$$

$$\Rightarrow \quad T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1} \quad \dots(2.82)$$

$$\Rightarrow \quad T_1 p_1^{\frac{1-\gamma}{\gamma}} = T_2 p_2^{\frac{1-\gamma}{\gamma}} \quad \dots(2.89)$$

Having learnt about the relationship between different thermodynamic properties for adiabatic expansion solve the following SAQ.

### SAQ 5

2.00 moles of an ideal monoatomic gas, undergo adiabatic reversible expansion from a volume of 22.4 dm<sup>3</sup> to double its volume at 0 °C. Calculate the final temperature and pressure of the gas.

[Given:  $C_{v,m} = 12.47 \text{ J K}^{-1} \text{mol}^{-1}$ ]

## 2.6 SUMMARY

In this unit we discussed about the First law of thermodynamics. In order to understand the law we introduced the concept of internal energy and developed the relationships between heat, work and internal energy. We rationalised the effect of heat and work on the system in terms of the changes in the internal energy. In the process we developed the mathematical expression for the first law of thermodynamics and also emphasised that while heat and work are path functions, the internal energy is a state function. The

application and the significance of the expression was clarified with the help of examples.

This was followed by discussion on the heat changes under constant volume conditions and realised the heat change accompanying a process under constant volume is related to the change in internal energy of the system.

While discussing heat changes under constant pressure conditions we introduced the concept of enthalpy - a thermodynamic quantity equivalent to the total heat content of a system. It is defined as the internal energy of the system plus the product of pressure and volume. It is a state function whose change is equal to the heat withdrawn from the surroundings in a process at constant pressure.

This was followed by the derivation of mathematical expressions for isothermal irreversible and reversible expansion of an ideal gas. In this context we derived expressions for isothermal expansion in one, two and infinite number of steps. The importance of these expressions was clarified with examples. Towards the end of the unit we formulated relationships between different state variables for ideal gas undergoing adiabatic expansion.

## 2.7 TERMINAL QUESTIONS

1. Give different statements of the First Law of thermodynamics.
2. Formulate the mathematical expression for the First law of thermodynamics.
3. A sample of an ideal gas expands from an initial volume of  $5.00 \text{ dm}^3$  to  $20.00 \text{ dm}^3$  against an opposing pressure of 1 bar. In addition, 800 J of heat is also transferred to the system. Calculate the change in the internal energy of the system.
4. Define state and path functions and give suitable examples for the same.
5. Show that the heat absorbed by a system at constant volume is equal to increase in internal energy of the system
6. 1.50 moles of gas behaving ideally at a pressure of 4 bar and temperature of 300 K undergo isothermal expansion against a constant pressure of 1 bar. How much of the work is done by the gas?
7. Calculate the work done for the following processes on a sample of 0.500 mole of nitrogen gas occupying a volume of  $5.00 \text{ dm}^3$  at 298 K
  - a) Expansion to  $10.00 \text{ dm}^3$  against a constant pressure of 1 bar
  - b) Isothermal reversible expansion to  $10.00 \text{ dm}^3$
8. 1.00 mole of helium gas at a temperature of  $100^\circ\text{C}$  is made to undergo reversible adiabatic expansion from an initial volume of  $4.00 \text{ dm}^3$  to  $20.00 \text{ dm}^3$ . Calculate the final temperature of the gas, assuming helium to behave ideally and has  $C_{V,m} = 12.47 \text{ J K}^{-1}\text{mol}^{-1}$

## 2.8 ANSWERS

### Self-Assessment Questions

1. According to the First Law of thermodynamics,  $\Delta U = q + w$

The amount of energy supplied to the system as heat,  $q = 416 \text{ J}$

The change in the internal energy,  $\Delta U = 268 \text{ J}$

Substituting in the equation we get,

$$268 \text{ J} = 416 \text{ J} + w$$

Solving we get,

$$w = -148 \text{ J}$$

As the value for  $w$  is non-zero, some work is associated with the system. Further, as the work comes out to be negative, it implies that the system has done work on the surroundings.

2. The enthalpy is a thermodynamic quantity equivalent to the total heat content of a system. It is defined as  $H = U + pV$ , i.e., the internal energy of the system plus the product of pressure and volume. It is a state function whose change ( $\Delta H$ ) is equal to the heat withdrawn from the surroundings in a process at constant pressure,  $q_p$ .

3. a) We know that for isobaric process (occurring at constant pressure), the heat required to raise the temperature is,  $q_p = nC_{p,m}\Delta T$ .

Given:  $C_{p,m} = 20.78 \text{ J K}^{-1}\text{mol}^{-1}$ ,  $n = 1.00 \text{ mol}$ ,  $\Delta T = 900 - 100 = 800 \text{ K}$

Substituting in the expression,

$$q_p = 1.00 \text{ mol} \times 20.78 \text{ J K}^{-1}\text{mol}^{-1} \times 800 \text{ K} = 16,624 \text{ J} = 16.624 \text{ kJ}$$

- b) Similarly, for isochoric process (occurring at constant volume), the heat required to raise the temperature is,  $q_v = nC_{V,m}\Delta T$

Given:  $C_{V,m} = 12.47 \text{ J K}^{-1}\text{mol}^{-1}$ ,  $n = 1.00 \text{ mole}$ ,  $\Delta T = 900 - 100 = 800 \text{ K}$

Substituting in the expression,

$$q_v = 1.00 \text{ mol} \times 12.47 \text{ J K}^{-1}\text{mol}^{-1} \times 800 \text{ K} = 9976 \text{ J} = 9.976 \text{ kJ}$$

4. The maximum work of expansion is given as

$$w_{\max} = -2.303 nRT \log \frac{V_2}{V_1}$$

The data given is as under:

$$n = 1.0 \text{ mol} \quad V_1 = 10.00 \text{ dm}^3 \quad V_2 = 20.00 \text{ dm}^3$$

$$T = 273.15 + 25 = 298.15 \text{ K}$$

Substituting the values in the expression, we get

$$w_{\max} = -2.303 \times 1.0 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K} \times \log \frac{20}{10}$$

$$= -1718.32 \text{ J} = -1.718 \text{ kJ}.$$

⇒ Thus a maximum work equal to 1.718 kJ is done by the gas on the surroundings

5. The temperature and volume for a reversible adiabatic expansion of an ideal gas are related as

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

To begin with we need to compute the value for,  $\gamma = \frac{C_p}{C_V}$

For ideal gas,  $C_p - C_V = R \Rightarrow C_p = R + C_V$

$$\Rightarrow C_p = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} + 12.47 \text{ J K}^{-1} \text{ mol}^{-1} = 20.784 \text{ J K}^{-1} \text{ mol}^{-1}$$

Substituting above we get,

$$\gamma = \frac{20.784}{12.47} = 1.667$$

Now we can compute,  $T_2$ ,  $T_1$  is given as  $0^\circ\text{C} = 273.15 \text{ K}$

Rearranging Eq. (2.81), we get,

$$T_2 = T_1 \left( \frac{V_1}{V_2} \right)^{\gamma-1}$$

Substituting the values,

$$T_2 = 273.15 \text{ K} \left( \frac{44.8 \text{ dm}^3}{22.4 \text{ dm}^3} \right)^{1.667-1}$$

Solving, we get  $T_2 = 433.70 \text{ K}$

Now, in order to find the final pressure we can simply use the ideal gas equation.

$$\text{From ideal gas equation, } p = \frac{nRT}{V}$$

$$\text{Substituting the values, } p = \frac{1.00 \text{ mol} \times 8.314 \text{ J K}^{-1} \times 433.70 \text{ K}}{22.40 \text{ dm}^3}$$

On solving,  $p_2 = 166.97 \text{ J dm}^{-3} = 1.67 \text{ bar}$

$$\Rightarrow 1 \text{ bar dm}^3 = 10^2 \text{ J} \quad \therefore 1 \text{ bar} = 10^2 \text{ J dm}^{-3}$$

Thus, the final temperature and pressure would be 433.70 K and 1.67 bar respectively.

## Terminal Questions

1. The First law of thermodynamics can be stated in a number of ways, some of these are
  - The total energy of universe is constant.
  - It is not possible to construct a machine showing perpetual motion of the first kind. That is, a machine, which can work endlessly without the expenditure of energy.
  - The internal energy of an isolated system is constant.
2. The mathematical expression for the First Law of thermodynamics can be formulated by more than one equivalent ways. As per one of the ways suppose we transfer  $+q$  amount of energy to the system as heat and if the system does  $w$  amount of work then we can write,

$$q = \Delta U + (-w)$$

This can be rearranged to give the mathematical expression for the first law as  $\Delta U = q + w$

3. According to the first law of thermodynamics,  $\Delta U = q + w$

We are given  $q = +800\text{ J}$  (positive sign indicates that the heat is supplied to the system)

We need to calculate the work done

The work of expansion against a constant opposing pressure is,

$$w = -p_{op} \Delta V$$

$$p_{op} = 1\text{ bar}, \Delta V = V_2 - V_1 = 20.00 - 5.00 = 15\text{ dm}^3$$

Substituting in the equation we get,

$$w = -1.00\text{ bar} \times 15\text{ dm}^3 = -15\text{ bar dm}^3$$

$$= -1500\text{ J} \quad (\because 1\text{ bar dm}^3 = 100\text{ J})$$

Substituting the values of heat and work in the expression for change in internal energy, we get,

$$\Delta U = 800\text{ J} + (-1500\text{ J}) = -700\text{ J}$$

The internal energy of the system would decrease by 700 J

4. A state function is the one whose value depends on the state of the system irrespective of how it is achieved. On the other hand, the path functions are the ones whose value depends on the path followed during the thermodynamic process. Internal energy, enthalpy, pressure, and temperature are some of the examples of state functions whereas the heat change and work associated with the process are path functions.

5. As per the first law of thermodynamics,

$$dU = dq + dw$$

As the heat is transferred under the conditions of constant volume, the term,  $dw$  is equal to zero and we can write,

$$dU = dq_V$$

This represents infinitesimal change in internal energy. We can get the finite change in internal energy at constant volume by integrating the equation as

$$\begin{aligned}\Delta U_V &= \int dU = \int dq_V = q_V \\ \Rightarrow \Delta U_V &= q_V\end{aligned}$$

Thus, the heat absorbed by a system at constant volume is equal to increase in internal energy of the system,

6. The work of expansion against a constant opposing pressure is given as

$$w = -p_{ext} \cdot \Delta V$$

Given:  $p_{op} = 1.00 \text{ bar}$      $n = 1.50 \text{ mol}$      $p_1 = 4.0 \text{ bar}$      $p_2 = 1.0 \text{ bar}$

In order to get the value of  $\Delta V$ , we take the help of the ideal gas equation,  $V = nRT/p$

$$\Delta V = V_2 - V_1 = \left( \frac{nRT}{p_2} - \frac{nRT}{p_1} \right) = nRT \left( \frac{1}{p_2} - \frac{1}{p_1} \right)$$

Substituting in the expression for  $w$ ,

$$\begin{aligned}w &= -p_{ext} \cdot \Delta V \\ &= -p_{ext} \cdot nRT \left( \frac{1}{p_2} - \frac{1}{p_1} \right) \\ &= -1.00 \text{ bar} \times 1.50 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{mol}^{-1} \times 300 \text{ K} \times \left( \frac{1}{1} - \frac{1}{4} \right) \text{ bar}^{-1}\end{aligned}$$

On solving, we get

$$w = +2806 \text{ J} = 2.806 \text{ kJ}$$

Thus, a work equal to 2.806 kJ would be done by the system.

7. a) The work of expansion against a constant opposing pressure,

$$w = -p_{ext} \cdot \Delta V$$

Given:  $p_{op} = 1.00 \text{ bar}$      $n = 0.50 \text{ mol}$      $V_1 = 5.00 \text{ dm}^3$      $V_2 = 10.00 \text{ dm}^3$

Substituting in the expression for  $w$ ,

$$\begin{aligned}w &= -P_{ext} \cdot \Delta V = -1.00 \text{ bar} \times (10.00 \text{ dm}^3 - 5.00 \text{ dm}^3) \\ &= -5.00 \text{ bar dm}^3 \\ &= -500 \text{ J} \quad (\because 1.00 \text{ bar dm}^3 = 100 \text{ J})\end{aligned}$$

- c) The work of isothermal reversible expansion is given as

$$w_{\text{Rev}} = -2.303 nRT \log \frac{V_2}{V_1}$$

Given:  $n = 0.50 \text{ mol}$      $V_1 = 5.00 \text{ dm}^3$      $V_2 = 10.00 \text{ dm}^3$      $T = 298 \text{ K}$

Substituting in the expression for  $w$ ,

$$w_{\text{max}} = -2.303 \times 0.50 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K} \times \log \frac{10.00}{5.00}$$

On solving, we get  $w = -858.73 \text{ J}$

Thus a work equal to 0.859 kJ would be done by the system.

8. We know that the temperature and volume for a reversible adiabatic expansion of an ideal gas are related as,

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

To begin with we need to compute the value for,

$$\gamma = \frac{C_p}{C_v}$$

For ideal gas,  $C_p - C_v = R \Rightarrow C_p = R + C_v$

$$C_p = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} + 12.47 \text{ J K}^{-1} \text{ mol}^{-1} = 20.784 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\text{Substituting above we get, } \gamma = \frac{20.784}{12.47} = 1.667$$

Now we can compute,  $T_2$ ,  $T_1$  is given as  $0^\circ\text{C} = 373.15 \text{ K}$

$$\text{Rearranging Eq. 2.81, we get, } T_2 = T_1 \left( \frac{V_1}{V_2} \right)^{\gamma-1}$$

$$\text{Substituting the values, } T_2 = 373.15 \text{ K} \left( \frac{20.0 \text{ dm}^3}{4.0 \text{ dm}^3} \right)^{1.667-1}$$

Solving, we get  $T_2 = 1091.68 \text{ K}$